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Emissions from Sewage Sludge Pyrolysis Oil and Gas Combustion and Influence of ZnCl_2/KOH

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Abstract

In this study, the combustion emission characteristics of pyrolysis oil and gas from raw sewage (SC-Raw), sewage with KOH activation (SC-KOH) and sewage with ZnCl_2 activation (SC- ZnCl_2) were analyzed and compared. The results indicated that the three kinds of sludge samples have the same pollutant release patterns following the combustion of corresponding pyrolysis oils and gases with oxygen-enriched air. CO_2 , SO_2 , NO_x , N_2O and HCl are the main pollutants, while CO , NH_3 , HCN and CH_3N accounted for a minor relative proportion. Compared to SC-Raw, SC-KOH and SC- ZnCl_2 can be effective in reducing acid gases, and most significantly the removal of SO_2 . Likewise, the pyrolysis process shows that more N_2O is released from SC-KOH, while SC- ZnCl_2 releases a considerable amount of HCl .

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1. Introduction

Sewage sludge treatment disposal is one of the most complex environmental problems. Generally, sludge disposal methods include landfill, composting, incineration, and pyrolysis [1]. Pyrolysis is used to convert sewage sludge into renewable resources (i.e. pyrolysis oils and gases) for the sustainable development of the environment and energy conservation. Compared to direct combustion of raw sludge, the combustion of pyrolysis oil and gas generated from the sewage sludge pyrolysis process is deemed as a cleaner process and more environmentally friendly. However, few studies have examined the combustion characteristics of pyrolysis oil and gas. In this work, the pyrolysis of oil and gas combustion exhaust of three types of pre-treated sewage sludge (SC-Raw, SC-KOH, SC- ZnCl_2), including CO_2 , CO , SO_2 , NO , NO_2 , N_2O , NH_3 , HCl , HCN , CH_3N are analyzed. Furthermore, the three sewage sludge chars obtained at pyrolysis temperatures of 650°C resulted into three different kinds of catalysts that could be reused in a future study.

2. Experimental materials and method

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(1) Production of activated char as catalysts

Nomenclature of the activated chars used in this study is summarized in Table 1.

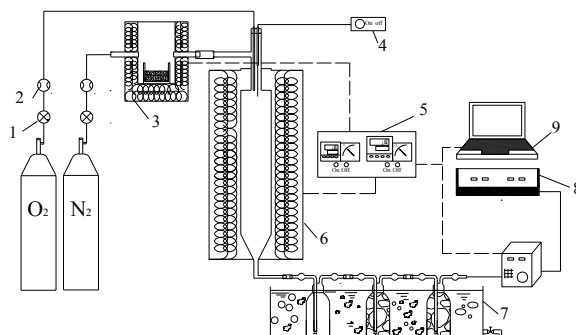
Table 1. Nomenclature of activated chars

	Active agent	Metal incorporation
SC-Raw	/	/
SC-KOH	KOH	/
SC-ZnCl ₂	ZnCl ₂	Fe(NO ₃) ₃ , Mn(NO ₃) ₂

For activation and metal incorporation, the solution consisting of ZnCl₂, Fe(NO₃)₃, and Mn(NO₃)₂ was implanted into the wet sludge sample for 6 hours by a rotary machine before it was dried completely. The ZnCl₂-to-dried sludge mass ratio and Zn²⁺-to-Fe²⁺ and Mn²⁺ mole ratios were 1:1 and 1:0.5. The KOH solution was implanted into the wet sludge with a 1:1 weight ratio for chemical activation. Then the mixed sewage sludge samples were dried for more than 24 hours in a 105°C oven.

(2) Combustion process and exhaust analysis

Figure 1 shows a schematic experimental apparatus, including a sewage sludge pyrolysis system, an online flue gas analysis system, and a reactor to simulate the combustion process of the pyrolysis gas and oil.



1. Reducing Valve; 2. Mass flowmeter; 3. Pyrolysis furnace; 4. Combustion furnace; 5. Controller; 6. Cl collection; 7. Sampling chamber; 8. Dx4000 flue gas analyzer; 9. Computer

Figure 1. Schematic diagram of the laboratory-scale experimental system

For the first part, shown in Figure 1, the pyrolysis experiments were performed at a prearranged temperature between 50 and 650°C in a crucible with sewage sludge samples heated by an electrical furnace and using N₂ as a sweeping gas. While performing the experiments, temperature measurements were taken with four thermocouples. For each experiment, a 10g sewage sludge sample was fed to the crucible and then the furnace was heated up to the selected final temperature. For the second part of the experiment, a drop tube steel reactor was heated at a temperature range of 680~700 °C by a two-zone electric furnace. A pure flow of O₂ at 1L/min was mixed with the combustible gas and oil made from the pyrolysis process in order to supply an oxygen-enriched combustion environment. Some by-products, particularly HCl from the steam, were collected in an ice-water bath; While the noncondensable gases from the reactor, such as O₂, CO, NO, N₂O, NO₂, SO₂ and HCN, were analyzed by an online fourier transform infrared spectrometer (Gasmeter DX4000) connected to a personal computer.

3. Results and discussion

(1) Emissions from different combustion modes

Figure 2 shows the combustion pollutants release performance of different samples, and Table 2 shows the HCl emission value of the three samples. These include a full range of pollutants, majorly: carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2), nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), ammonia (NH_3), hydrogen cyanide (HCN), methylamine (CH_3N), hydrogen chloride (HCl) as well small traces of other pollutants. From Figure 2 and Table 2 it can be observed that the three kinds of sludge samples have the same pollutant release patterns following the combustion of the corresponding pyrolysis oils and gases with oxygen-enriched air. CO_2 , SO_2 , NO_x , N_2O and HCl are the main pollutants, while CO , NH_3 , HCN and CH_3N accounted for a minor relative proportion.

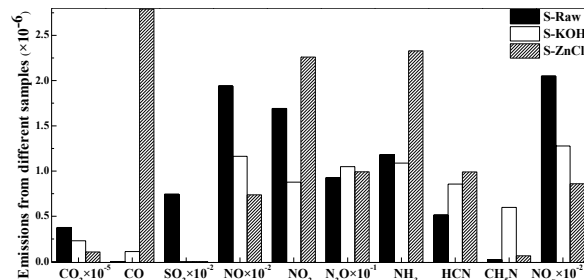


Figure 2. Average emission from different sewage sludge samples

Table 2. Average emission of HCl ($\times 10^{-6}$)

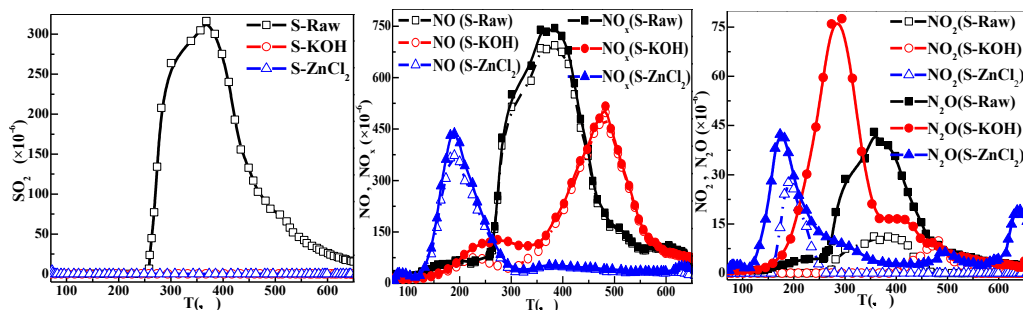
SC-Raw	SC-KOH	SC-ZnCl ₂
52.6	39.9	739.5

As observed from Figure 2, the quantities of pollutants CO_2 , SO_2 , and NO_x are mainly found in SC-Raw, followed by SC-KOH, with the least pollutants detected in SC-ZnCl₂. The most obvious decrement among these three pollutant gases is SO_2 . SO_2 emission from SC-Raw is about 800×10^{-6} , while SC-KOH and SC-ZnCl₂ did not release SO_2 , showing that both could play an effective role in sulphur fixation. This is because adding KOH to the sludge will make SC-KOH alkaline enabling it to absorb the acidic gases CO_2 , SO_2 and NO_x ; SC-ZnCl₂ although not alkaline, is rich in metal ions, hence when ZnCl_2 is added to the sludge, it will bind acid gas to form carbonate, sulphate, nitrate salts which will be stored in SC-ZnCl₂ carbon. Among these salts, sulphates are relatively stable. Pyrolytic reduction reaction occurs only in a reducing atmosphere and close to 800°C , with H_2S being generated in the process [2]. Therefore, the release of acid gases of these two types of sludge with additives (SC-KOH and SC-ZnCl₂) is much less than that of the original sludge (SC-Raw).

From the figures in Table 2, the HCl releases of SC-Raw and SC-KOH show little difference, while for SC-ZnCl₂ the HCl release is fifteen times higher than the former, mainly because the added ZnCl_2 in the pyrolysis process creates a substantial release of HCl , causing the HCl combustion gases to increase dramatically.

(2) Releasing rules of combustion pollutants of oils and gases from sludge pyrolysis

Figure 3 shows the SO_2 , NO/NO_x , $\text{NO}_2/\text{N}_2\text{O}$ release patterns for the three sludge samples. Figure 3 displays the emission patterns of the different compounds as a function of pyrolysis temperature and reveals the levels of pollutant release during the pyrolysis processes of different types of carbon sludge.



(a) SO₂ (b) NO, NO_x (c) NO₂, N₂O
Figure 3. Emission laws of different compounds as a function of pyrolysis temperature

From Figure 3 (a), SC-Raw begins to release SO₂ at pyrolysis temperature 250 °C, reaching a maximum release of SO₂ at 400°C, and then gradually decreases to 500×10^{-6} or less at temperatures higher than 600°C. SC-KOH and SC-ZnCl₂ does not release SO₂ through the whole process, this shows that adding KOH or ZnCl₂ and some metal salts in the sludge at any tested temperature can inhibit SO₂ emissions.

From Figure 3 (b), NO/NO_x released from SC-Raw first remains stable before 250 °C, and starts to rise sharply to a maximum of 750×10^{-6} , and then begins to decrease, implying that the maximum release period is somewhere between 250~500 °C. The results from SC-KOH show little NO/NO_x release before 350 °C, while in the range of 350~550 °C, the maximum volume release of NO/NO_x is lower than the levels of SC-Raw. It was also found that NO/NO_x emissions of SC-ZnCl₂ were lower than that of the previous two kinds of sludge. NO/NO_x release from the SC-ZnCl₂ peaks at 150~250 °C, after 300 °C it remains stable, showing no more than 50×10^{-6} . The NO emission of SC-ZnCl₂ below 300 °C is due to the pyrolysis of nitrates Fe(NO₃)₃, and Mn(NO₃)₂ pre-treated into SC-ZnCl₂. While SC-Raw and SC-KOH generating NO at a higher temperature are mostly due to the decomposition of N and O from the macromolecular structure of its own organic sludge.

Figure 3 (c) shows SC-ZnCl₂ has the most NO₂ emission among the three kinds of sludge. This is mainly due to the decomposition of nitrates at the low temperature range. The N₂O released from the three kinds of sludge is not the same, SC-Raw and SC-ZnCl₂ release almost the same amount of N₂O. The maximum values being both around 40×10^{-6} , but N₂O discharged from SC-KOH is twice as much as the other two. This is because adding KOH will increase the pH of the sludge, thus promoting the nitrifying activity of the sludge [3]. Another explanation perhaps is that some intermediate products such as NH₂OH and NO₂⁻-N [4] lead to a large quantity of N₂O production during the pyrolysis process.

4. Conclusions

Based on the results of the research on emissions from sewage sludge pyrolysis oil and gas combustion, and the influence of ZnCl₂/KOH, the following conclusions can be drawn:

- (1) The main pollutants from the combustion of sewage sludge pyrolysis oils and gases were CO₂, SO₂, NO_x, N₂O and HCl. SC-KOH and SC-ZnCl₂ can be effective in reducing acid gases including SO₂ and NO/NO_x.
- (2) The HCl releases from SC-Raw and SC-KOH have no significant difference, while HCl release in SC-ZnCl₂ is 15 times higher than the other two types of sludge.
- (3) SC-Raw and SC-ZnCl₂ released almost the same amount of N₂O, the maximum values are both around 40×10^{-6} , but N₂O emission from SC-KOH is twice as much as the other two types of sludge.

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